Arylcyclopropane Photochemistry. Part 4.[1] The Photochemistry of Some 2-Arylcyclopropanecarboxylates

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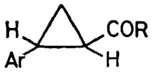
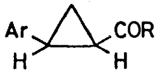
The photochemistry of some 2-arylcyclopropanecarboxylates has been studied. Both the direct (λ 254 nm) and triplet-sensitized (λ 313 nm) irradiation of the *trans*-isomers yields only the corresponding *cis*-isomers. The direct irradiation of methyl *cis*-2-phenylcyclopropanecarboxylate and of *cis*-2-phenylcyclopropanecarboxylic acid yields products which are formed *via* 1,3-dipolar intermediates. The difference in photoreactivity between these *cis*-isomers and their *trans*-isomers is explained in terms of intramolecular exciplex formation with the *cis*-isomers which cannot occur with the *trans*-isomers. The difference in photoreactivity between the *cis*-compounds without a methoxy-group (2a,b) and those with a methoxy-group attached to the phenyl nucleus (2c,d) is explained in terms of the occurrence of a chemical reaction of the intramolecular exciplex of (2a,b) and the non-occurrence of any chemical reaction of the intramolecular exciplex of (2c,d). The intramolecular exciplex formation with the methoxy-substituted *cis*-compounds (2c,d) only leads to an increased ϕ_{iec} of these *cis*-compounds relative to that of the corresponding *trans*-isomers (1c,d).

As part of our programme of work on the photochemistry of arylcyclopropanecarboxylates[1] we have examined the photochemistry of some 2-arylcyclopropanecarboxylates. *A priori* one expects that these photo-excited substrates exhibit heterolytic cyclopropane bond cleavage with formation of a mesomerically stabilized zwitterion. Heterolytic cyclopropane bond cleavage was suggested before in order to explain the products formed on irradiation of 2-arylcyclopropylcarbinols and their acetates;[2] however it proved difficult to explain the effect of substituents of the phenyl ring on the photoreactivity in terms of mesomeric stabilization of the intermediate zwitterion. The observed effects of the phenyl substituents on the photoreactivity were therefore ascribed to the difference in electronic effects in the ground and excited state of the substituted phenyl moiety.[2]

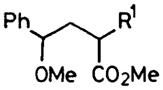


(1)

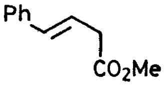


(2)

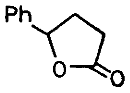
a; Ar = Ph, R = OMe
b; Ar = Ph, R = OH
c; Ar = p-MeOC$_6$H$_4$, R=OEt
d; Ar = m-MeOC$_6$H$_4$, R=OEt
e; Ar = p-MeOC$_6$H$_4$, R=OH
f; Ar = p-MeOC$_6$H$_4$, R=OK



(3)
a; R^1=H
b; R^1=D



(4)



(5)

RESULTS AND DISCUSSION

Synthesis of Starting Materials.—Methyl *trans*-2-phenylcyclopropanecarboxylate (1a) was obtained by reaction of the corresponding chloride with methanol.

Ethyl 2-(*p*-methoxyphenyl)cyclopropanecarboxylate was obtained as *cis–trans* mixture, (1c) and (2c), upon reaction of ethyl diazoacetate and *p*-methoxystyrene,[3] although this reaction was reported to yield exclusively the *trans*-isomer (1c).[3]

Ethyl 2-(*m*-methoxyphenyl)cyclopropanecarboxylate, (1d) and (2d), was obtained similarly, starting from *m*-methoxystyrene.

Irradiation of (1a) *and* (1b).—Irradiation (λ 254 nm) of (1a) (1.2 mmol) in dry methanol (6 ml) for 60 h led to the formation of (2a), (3a), and (4), together with substantial amounts of polymer, as was concluded from the dark yellow colour of the irradiated solution, and the large difference in total g.l.c. peak area before and after the irradiation.† Upon irradiation of (1a) in dry benzene or acetonitrile only (4) is formed. The esters (3b) and (4) are formed upon direct irradiation of (1a) in CH_3OD. Upon acetone-photosensitized irradiation (λ 300 nm) (1a) gave only *trans–cis*-isomerization which eventually led to a photostationary state $(1a)/(2a)_{pss} = 1.2$.

Irradiation (λ 254 nm) of the acid (1b) (1.83 mmol) in benzene (12 ml) for 12 h afforded, after removal of all acidic material, compound (5) (*ca.* 0.1 mmol).

There is a striking difference in the dependence of the formation of (3a) and (4) on irradiation time for the λ 254 nm irradiation of pure (1a) (Figure 1) and for that of a mixture of (1a) and (2a) (Figure 2). In Figure 1 there is an induction period for the formation of (3a) and (4), whereas in Figure 2 there is not. Accordingly, (3a) and (4) are (at least mainly) formed by reaction from an excited state of (2a) and not (or at most to a minor extent) from an excited state of (1a). These excited

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† Compounds (1a) and (2a) had identical g.l.c. retention times, and were, therefore, isolated together. The mixture proved to contain 39% of (2a), based on the relative ^{1}H n.m.r. absorbtions, especially on those of the methyl groups.

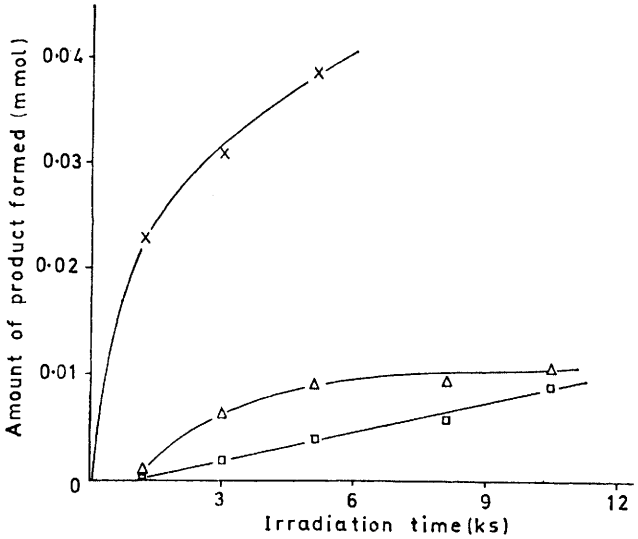


FIGURE 1 Dependence of the formation of (3a) and (4) on the irradiation time for the λ 254 nm irradiation of (1a) (0.393 mmol) in methanol–benzene (5 ml, 6 : 4 v/v); × = consumed (1a) + (2a), Δ = (3a), □ = 4

states must be singlet states, as (3a) and (4) were not formed upon acetone triplet photosensitization.

The difference in photoreactivity of (1a) and (2a) suggests that the products (3) and (4) result from a singlet excited state of the *cis*-isomer (2a) in which there is interaction between the ester group and the singlet excited state of the phenyl moiety. With (1a), in which the ester group is *trans* to the phenyl group, this interaction is not possible for geometric reasons. The fluorescence of phenylacetic acid is quenched by a charge-transfer (CT) from the singlet-excited phenyl group to the carbonyl group.[4] Therefore we propose that the ^1S state formed upon direct irradiation of (2a) yields the exciplex ^1E which has some CT character which eventually yields the observed photoproducts (see Scheme). We propose that the zwitterion is formed from the exciplex *via* a diradical zwitterion and not directly from the exciplex, as the former possibility enables us to explain also our results with (1c), (1d), (2c), and (2d) (see later). In the absence of an alkanol the zwitterion only rearranges to (4). In the presence of an alkanol the zwitterion is in addition trapped with formation of (3).

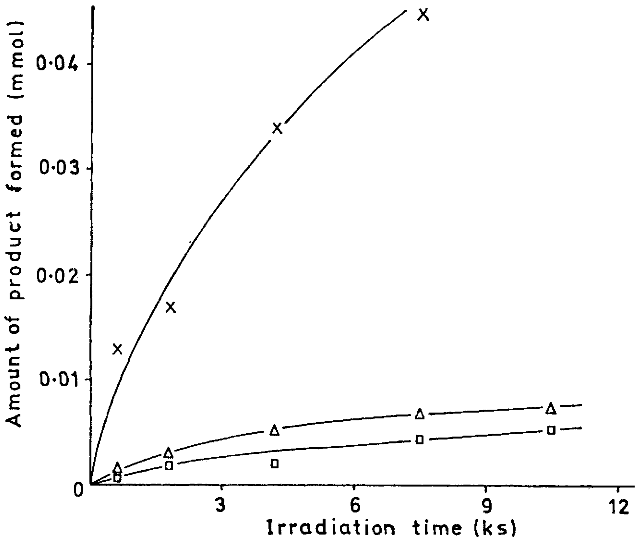
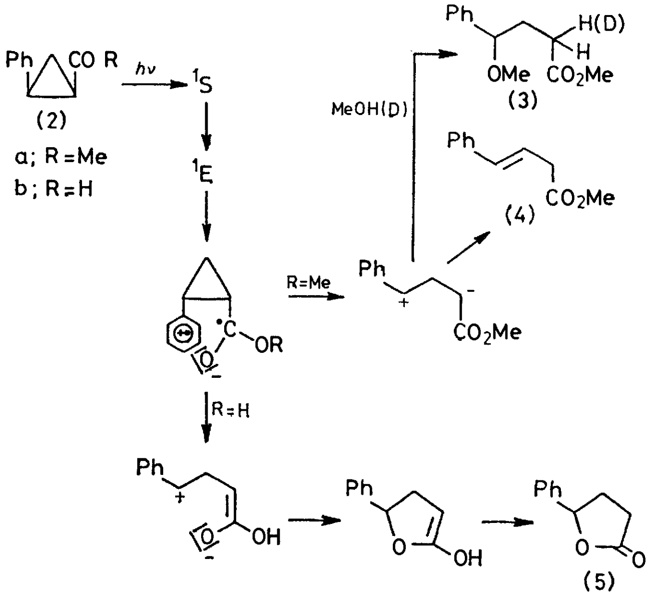


FIGURE 2 Dependence of the formation of (3a) and (4) on the irradiation time for the λ 254 nm irradiation of a mixture of (1a) (0.243 mmol) and (2a) (0.146 mmol) in methanol–benzene (5 ml; 6 : 4 v/v); × = consumed (1a) + (2a), Δ = (3a), □ = 4

The photoformation of (5) from (1b) can also be explained in terms of a zwitterionic intermediate (Scheme). By analogy with the mechanism for the formation of (3) and (4) from (2a), it is proposed that (5) is only formed from singlet excited (2b), and not from singlet excited *trans*-isomer (1b).

The Irradiation of (1c), (2c), (1d), *and* (2d).—These substrates have been examined because the methoxy-group of (2c) and (2d) would, respectively, mesomerically stabilize and inductively destabilize an intermediate zwitterion relative to that resulting from (2a).



SCHEME

Upon acetone triplet-sensitized irradiation (1c) and (1d) only exhibited *trans–cis* isomerization with an eventual photostationary *trans–cis* ratio $[(t/c)_{pss}]$ of 1.15 and 1.25 respectively. These values are close to the (1a)/(2a)$_{pss}$ ratio of 1.2 (see before). Upon direct irradiation (λ 254 nm) of both (1c) and (1d) in methanol as a solvent only *trans–cis* isomerization was observed. The absence of any product derived from a zwitterionic intermediate infers that one of the three steps leading to the zwitterion (see Scheme) does not take place.

In order to obtain information as to which step does not occur, it was necessary to study the fluorescence of these substrates. The compounds (1c), (2c), (1d), (2d), (2e), and (2f) in acetonitrile as a solvent exhibited fluorescence, with a maximum emission in between 300 and 305 nm; for *p*-methoxytoluene it is at 299 nm.

Accordingly, the fluorescence is considered to result from the substrates with excitation located in the aryl group. The ratio of the fluorescence intensity of (1c) and (2c)*, and of (1d) and (2d)* are collected in Table 1.

TABLE 1

Photochemical and photophysical data of (1c), (2c), (1d), and (2d)

Ar	$(t/c)^{\lambda\,254\,\text{nm}}_{\text{pss}}$	$(\varepsilon_t/\varepsilon_c)$ λ 254 nm	$\phi_f(1)/\phi_f(2)$
p-MeOC$_6$H$_4$	0.42 [a]	0.67 [b]	9.0 [b]
m-MeOC$_6$H$_4$	0.67 [a]	1.0 [b]	3.0 [b]

[a] Methanol solution. [b] Acetonitrile solution.

That of (2f) and (2e) for water as a solvent was found to be 7.5. The fluorescence intensity of (1c) was found to be only 32% of that of *p*-methoxytoluene. This can be explained in terms of the additional singlet-excited state deactivation of (1c) by cyclopropane bond homolysis.[5,6] The fluorescence intensity of the acid (2e) is much lower than that of its anion. It is concluded therefore that the singlet excited state of (2e) gives an intramolecular exciplex in contrast to that of (2f) which does not; the latter is explained in terms of the poor electron acceptor properties of the carboxylate anion;[4] similar reasoning was advanced to explain the difference in fluorescence intensity between phenylacetic acid and its carboxylate anion. From the data for $\phi_f(1)/\phi_f(2)$ (Table 1) it then follows that the *cis*-isomers (2c) and (2d) also exhibit exciplex formation, and that the major reason for the large difference in fluorescence intensity of (2c) and (1c) is the possibility of intramolecular exciplex formation in the case of (2c). A minor effect may be the difference in rate constant for the cyclopropane bond homolysis of the singlet excited state of (2c) (*cis*) and (1c) (*trans*). This rate constant has been estimated to be *ca.* 30% larger for (2c) than for (1c) on the basis of the fluorescence data of Table 2 and the fluorescence intensity of (1c) relative to that of *p*-methoxytoluene (= 0.32); the assumption was made that the ethoxycarbonyl group is as good an electron acceptor as the carboxylic acid group. The (calculated) higher rate constant for cyclopropane bond homolysis of (2c) as compared with (1c) may be explained in terms of steric acceleration, due to relief of strain between the aryl and the ester group of (2c).

It can be shown that the $(t/c)_{\text{pss}}$ for the direct (λ 254 nm) and for the sensitized irradiation of a 2-substituted 1-arylcyclopropane are related by equation (1) in which ϕ_{isc} is the quantum yield for excited singlet–triplet intersystem crossing.

$$\left(\frac{t}{c}\right)^{\lambda\,254\,\text{nm}}_{\text{pss}} = \frac{\varepsilon_c^{244\,\text{nm}}}{\varepsilon_t^{254\,\text{nm}}} \times \frac{\phi^c_{\text{isc}}}{\phi^t_{\text{isc}}} \times \left(\frac{t}{c}\right)^{\text{sens}}_{\text{pss}} \qquad (1)$$

Using the data for $(t/c)^{\text{sens}}_{\text{pss}}$ (see before) and those of Table 1, it was calculated that $\phi^c_{\text{isc}}/\phi^t_{\text{isc}}$ is 0.24 for (2c) and (1c), and 0.53 for (2d) and (1d). By using the fluorescence data of Table 1 and on the assumption that $k^c_{\text{isc}} = k^t_{\text{isc}}$, it was calculated that $\phi^c_{\text{isc}}/\phi^t_{\text{isc}}$ is 0.11 and 0.33 for (1c), (2c) and (1d), (2d) respectively. These values are smaller than those obtained from the photochemical data. This is ascribed to the value for the predicted ϕ^c_{isc} being too low. The higher observed value for ϕ^c_{isc} can, at least in part, be explained by an extra route for triplet population for the *cis*-isomer, *i.e.* intersystem crossing *via* an intramolecular exciplex, a route which was also proposed to account for the observed photophysical behaviour of phenylacetic acid.[4]

An alternative explanation for the difference between the observed and the predicted $\phi^c_{\text{isc}}/\phi^t_{\text{isc}}$ values would be intersystem crossing of the diradical intermediate, formed from the excited singlet state by cyclopropane bond homolysis, as advanced for some phenylcyclopropanes.[6] However, the small difference between the rate constants for cyclopropane bond homolysis of (*cis*)-(2c) and (*trans*)-(1c)($k^c/k^t = 1.3$, see before) cannot account for the large difference between the observed and predicted $\phi^c_{\text{isc}}/\phi^t_{\text{isc}}$ values, and renders the alternative explanation, accordingly, unlikely. This leaves the exciplex mechanism to be explained. The decay of the excited singlet state of the *cis*-isomers (2c) and (2d) to the products may now be represented by the following scheme, in which S^1_{Ar} and T^1_{Ar} denote the singlet and triplet states with excitation located in the aryl group, E^1 and E^3 the singlet and triplet intramolecular exciplex, and $\text{S}^1_{\text{birad}}$ and $\text{T}^1_{\text{birad}}$ denote the singlet and triplet states of the 1,3-diradical formed by cyclopropane bond homolysis.[6] For the *trans*-isomers (1c) and (1d) a similar scheme applies, however, without the exciplex route (steps 5, 6, and 7). The enhanced dissociation of the exciplexes *cis*-E^1 and *cis*-E^3 to a diradical zwitterion would relatively decrease the importance of the exciplex route for formation of *cis*-T^1_{Ar} from *cis*-S^1_{Ar} (steps 5, 6, and 7) and would thus decrease the $(t/c)_{\text{pss}}$ value for the direct (λ 254 nm) irradiation. For the case of complete exciplex quenching by dissociation (*i.e.* $v_7 = 0$) it was calculated using the predicted $\phi^c_{\text{isc}}/\phi^t_{\text{isc}}$ values (see earlier) that $(t/c)^{\lambda\,254\,\text{nm}}_{\text{pss}}$ will be 0.20 for (1c) and (2c) and 0.40 for (1d) and (2d). The $(t/c)_{\text{pss}}$ values for the direct irradiation (λ 254 nm) of (1c) in various solvents are collected in Table 2. With (1d) polymer formation is an important side reaction, and prevented the determination of the $(t/c)_{\text{pss}}$ values.

$$\begin{tikzcd}
 & \textit{cis}\text{-S}^1{}_{\text{birad}} \arrow[r, "4"] & \textit{cis}\text{-T}^1{}_{\text{birad}} \arrow[r] & \textit{cis}\text{-S}^0 + \textit{trans}\text{-S}^0 \\
\textit{cis}\text{-S}^0 \arrow[r, "h\nu"] & \textit{cis}\text{-S}^1{}_{\text{Ar}} \arrow[u, "3"'] \arrow[r, "1"] \arrow[d, "5"'] & \textit{cis}\text{-T}^1{}_{\text{Ar}} \arrow[u, "2"] & \\
 & \textit{cis}\text{-E}^1 \arrow[r, "6"] & \textit{cis}\text{-E}^3 \arrow[u, "7"] &
\end{tikzcd}$$

The $(t/c)^{\lambda\,254\,\text{nm}}_{\text{pss}}$ depends on the solvent (Table 2). However there appears to be no simple correlation between the $(t/c)^{\lambda\,254\,\text{nm}}_{\text{pss}}$ and the dielectric constant ε or Dimroth's solvent parameter E. It is to be expected

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* A change of the solvent from acetonitrile to cyclohexane did not alter the $\lambda_{\text{max.}}$ and the ratio of the fluorescence intensity of the *trans*- and *cis*-isomers. No exciplex emissions have been observed in these two solvents.

TABLE 2

Dependence of $(t/c)_{pss}$ for the direct irradiation (λ 254 nm) of (1c) on the solvent.[a]

Solvent	$(t/c)_{pss}$	ε^7	E^7
Cyclohexane	0.51	2.023	31.2
THF	0.32	7.58	37.4
t-Butyl alcohol	0.50	12.47	43.9
MeCN	0.38	37.5	46.0
MeOH	0.42	32.70	55.5

[a] E and ε stand for Dimroth's solvent parameter and the dielectric constant respectively.

that the exciplex dissociation is favoured in solvents with a high solvating ability for polar species. Accordingly it must be concluded that dissociation of the exciplex (E^1 or E^3) with formation of a diradical zwitterion does not occur to any appreciable extent at least with the solvents employed. The absence of any product which would result from dipolar addition of methanol to the cyclopropane ring may now be explained in terms of the absence of a diradical zwitterion.

The fluorescence quenching by intramolecular exciplex formation is more important for (2c) than for (2d) (Table 1) [the fluorescence intensities of (2c) and (2d) are almost equal].

The CT absorption band maximum of *p*-methoxytoluene–TCNE complex is at longer wavelength than that of *m*-methoxytoluene–TCNE.[8] This shows that *p*-methoxytoluene is a better electron donor than *m*-methoxytoluene. It must be stressed, however, that this does not have to be the case in the excited state as *p*-methoxytoluene absorbs at longer wavelength than *m*-methoxytoluene (the difference in absorption band location is *ca.* 5 nm.[9]). This infers that the difference in fluorescence quenching between (2c) and (2d) cannot be explained in terms of differences in electron-donating abilities. But the differences in fluorescence quenching of (2c) and (2d) match the predictions of a simple, qualitative MO description, based on the presence of bonding and anti-bonding interactions only, in the following way.†

It has been pointed out by Salem that, for a reaction between a photoexcited molecule (A*) and a ground-state molecule (B) to be favourable, strong interaction must be possible between the lowest unoccupied MO of B (LUMO) and the highest semi-occupied MO of A* (SOMO*), and between the highest occupied MO of B (HOMO) and the lowest semi-occupied MO of A* (SOMO).[11] The SOMO* and SOMO of photo-excited anisole are shown in Figure 3.‡ Dreiding model studies of (2c) showed that there will be orbital interaction between the molecular orbitals of the ester group and the atomic orbitals at C(3) and C(4), or at C(4) and C(5). For (2c), these two types of interaction are identically due to the C_{2v} symmetry of the *p*-methoxyphenyl group. The HOMO–SOMO combination affords two bonding interactions only, and the LUMO–SOMO* combination affords a bonding interaction at C(3), and a non-bonding one at C(4). With (2d), in which the cyclopropyl group is located at C(3), two different ways of complexation of the carbonyl group are possible. The one with C(3) and C(4) will give the same type of interactions as for (2c). For complexation at C(2) and C(3) the LUMO–SOMO* combination affords two bonding interactions only and the HOMO–SOMO combination a bonding and an anti-bonding interaction. Accordingly, with (2d) complexation of the ester group at C(2)–C(3) is suggested to be less favourable than complexation of the ester group of (2c) at C(4)–C(5); complexation at C(3)–C(4) is equally favoured for (2c) and (2d). Thus intramolecular exciplex formation may be predicted to be less favourable for (2d) than for (2c), which is, in fact, reflected by the fluorescence data (Table 1).

Conclusion.—The present results show that the singlet excited state of (1a) gives only rise to geometric isomerization. The singlet excited state of (2a), however, yields also an intramolecular exciplex, which gives after discociation of E^1 and subsequent cyclopropane bond homolysis a zwitterion. In the absence of an alkanol this intermediate rearranges to (4), whereas in the presence of an alkanol it is further in part trapped with formation of (3). The formation of (5) from singlet excited (1b) was also tentatively explained in terms of reaction *via* an exciplex. Like (1a), singlet excited (1c) and (1d) give only geometric isomerization. It was concluded from the fluorescence measurements that exciplex formation does occur with singlet excited (2c) and (2d). The apparently enhanced rate of intersystem crossing of (2c) relative to (1c) and of (2d) relative to (1d) has been explained in terms of an additional route for intersystem crossing *via* the intramolecular exciplexes of (2c) and (2d). The absence of any product which would result from a zwitterionic intermediate upon irradiation of (2c) and (2d) has been explained by the absence of dissociation of the exciplex

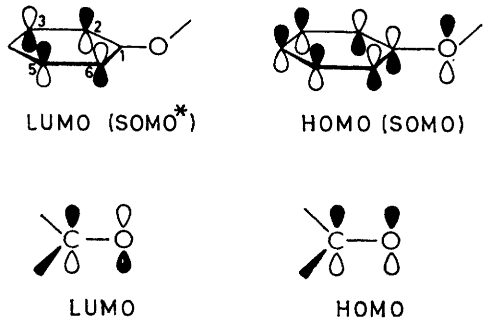

FIGURE 3 HOMO and LUMO of anisole and acetone

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† One of the photoproducts of 3,5-dimethoxybenzyl acetate is 6-acetoxy-1,3-dimethoxy-5-methylenecyclohexa-1,3-diene.[10] Its formation could infer a bonding interaction between the oxygen of the carbonyl group and C(2) of the aryl group in the excited state from which the cyclohexadiene is formed.

‡ For our qualitative reasoning the atomic orbitals have for reasons of simplicity all been given the same absolute orbital coefficients.

E[1] of (2c) and (2d), which was concluded from the solvent dependence of $(t/c)_{\text{pss}}^{\text{direct}}$.

The photoformation of (3) and (4) from (2a), and of (5) from (2b) is the second example of a photochemical reaction *via* an exciplex of a phenylalkanecarboxylic acid derivative. The first example is the photoformation of *p*-methoxybenzyl acetate from *p*-methoxyphenylacetic anhydride, which was recently reported and was also explained in terms of exciplex formation.[12] In addition, the recently reported (ionic) cyclopropylcarbinyl–homoallyl photorearrangements of some 2-arylcyclopropylcarbinols and acetates [2] may be explained in terms of an intramolecular exciplex of the *cis*-isomers as one of the intermediates (the *cis*-isomer of one of the carbinols was reported to rearrange *via* an ionic mechanism seven times faster than the *trans*-isomer,[2] for which intramolecular exciplex formation is impossible). The observed phenyl substituent effects on the photoreactivity of the 2-arylcyclopropylcarbinyl acetates [2] may thus also be explained in terms of differences in the exciplex formation and dissociation as a result of differences in the substituents of the phenyl groups.

EXPERIMENTAL

Materials.—The synthesis of (1c) and (2c) was carried out as described,[3] starting from *p*-methoxystyrene (74.6 m mol). Distillation after termination of the reaction afforded 5.9 g (72%) of a yellow oil which according to g.l.c. analysis consisted of a 2.4 : 1 mixture of (1c) and (2c). Careful addition of n-pentane afforded 2.0 g of crystalline (1c) (m.p. 82—83 °C). The ester (2c) was isolated from the mother liquor by preparative g.l.c.

The synthesis of (1d) and (2d) was carried out as for (1c) and (2c), starting from 3-methoxystyrene (74.6 mmol). Distillation (100—120 °C/0.005 mmHg) afforded 4.4 g (53%) of 2.3 : 1 mixture of (1d) and (2d). Separation of (1d) and (2d) was achieved by chromatography on a silica-gel column using 5% ethyl acetate in cyclohexane as eluants.

Irradiations.—The λ 254 and 300 nm irradiations were carried out in a Rayonet photochemical reactor type RPR 204 equipped with four RUL 253.7 nm lamps (using quartz vessels) and type RPR 208 with eight RUL 300 nm lamps (using Pyrex vessels) respectively. The photoreactions were monitored by g.l.c. analysis on a copper column (3.5 m, ¼ in, 150 °C, 12% OV-225 on Chromosorb W-AW 60—80 mesh, He flow rate 60 ml/min).

Fluorescence Measurements.—The spectra were recorded on a Shimadzu RF 500 spectrofluorometer.

Analysis.—^{1}H N.m.r. spectra were taken in $CDCl_3$, chemical shifts (δ) are given in p.p.m.; i.r. spectra were taken in $CHCl_3$, wavenumbers are given in cm^{-1}.

(1a): ^{1}H n.m.r.: 7.25 (m, 5 H, arom.), 3.71 (s, 3 H, Me), and 2.5—1.0 (m, 4 H, cyclopropyl H); i.r.: 1 720.

(2a): ^{1}H n.m.r.: 7.25 (m, 5 H, arom.), 3.42 (s, 3 H, Me), and 2.5—1.0 (m, 4 H, cyclopropyl H).

(1b): ^{1}H n.m.r.: 7.25 (m, 5 H, arom.) and 2.5—1.0 (m, 4 H, cyclopropyl H); i.r.: 2 900 and 1 720.

(1c): ^{1}H n.m.r.: 6.85 (m, 4 H, arom.), 4.15 (q, 2 H, CH_2), 3.75 (s, 3 H, Me), 2.40, 1.73, 1.45, and 1.15 (4 × m, 4 H, cyclopropyl H), and 1.2 (t, 3 H, Me); i.r.: 1 720.

(2c): ^{1}H n.m.r.: 7.0 (m, 4 H, arom.), 3.88 (q, 2 H, CH_2), 3.75 (s, 3 H, Me), 2.50, 2.00, 1.65, and 1.25 (4 × m, 4 H, cyclopropyl H), and 1.0 (t, 3 H, Me); i.r.: 1 720.

(1d): ^{1}H n.m.r.: 7.2—6.6 (m, 4 H, arom.), 4.13 (q, 2 H, CH_2), 3.74 (s, 3 H, Me), 2.5, 1.85, 1.55, and 1.25 (4 × m, 4 H, cyclopropyl H), and 1.21 (t, 3 H, Me); i.r.: 1 720.

(2d): ^{1}H n.m.r.: 7.2—6.6 (m, 4 H, arom.), 3.88 (q, 2 H, CH_2), 3.75 (s, 3 H, Me), 2.5, 2.0, 1.65, and 1.25 (4 × m, 4 H, cyclopropyl H), and 0.95 (t, 3 H, Me); i.r.: 1 720.

(3a): ^{1}H n.m.r.: 7.3 (m, 5 H, arom.), 4.12 (t, 1 H, benzylic H), 3.72 (s, 3 H, Me), 3.26 (s, 3 H, Me), 2.42 (t, 2 H, CH_2), and 2.10 (m, 2 H, CH_2); i.r.: 1 740.

(3b): ^{1}H n.m.r.: 7.3 (m, 5 H, arom.), 4.18 (t, 1 H, benzylic H), 3.74 (s, 3 H, Me), 3.22 (s, 3 H, Me), 2.40 (t, 1 H, CHD), and 2.05 (t, 2 H, CH_2).

(4): ^{1}H n.m.r.: 7.3 (m, 5 H, arom.), 6.6—6.2 (m, 2 H, *trans* CH=CH, J = 16 Hz), 3.44 (s, 3 H, Me), and 3.25 (d, 2 H, CH_2); i.r.: 1 720, 1 600, 1 580, and 1 500.

(5): ^{1}H n.m.r.: 7.25 (m, 5 H, arom.), 5.50 (t, 1 H, benzylic H), and 2.6 (m, 4 H, $(CH_2)_2$); i.r.: 1 775, 1 600, and 1 500.

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